

Application of X-ray Fluorescence and
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THE APPLICATION OF X-RAY FLUORESCENCE AND DIFFRACTION TO THE
CHARACTERIZATION OF ENVIRONMENTAL ASSESSMENT SAMPLES

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INTRODUCTION

The Technical Support Staff is called upon for analysis of a wide variety of sample types many of which have little sample history. However, it is usually necessary to account for all elements present. For these reasons, x-ray fluorescence spectrometry (XRF) has been a useful tool. Unfortunately, XRF requires the use of a range of standards for each element, the preparation of which could become so time consuming that the advantages of XRF would soon be diluted. Consequently, the utility of the J.W. Criss fundamental parameters computer program¹ was evaluated for samples in which only one standard per element was used and where the standard matrix did not strictly resemble the unknown matrix. Some of the results of these tests on environmental assessment samples are reported here.

The environmental significance of a sample is dependent not only on its elemental composition, but also on the species or phases which the elements comprise. X-ray powder diffraction (XRD) may be used to advantage for speciation. It will be seen that multi-phase environmental assessment samples are amenable to XRD interpretation. This may be performed using the Joint Committee on Powder Diffraction Standards (JCPDS) Hanawalt or Fink manual search methods² (tedious for multi phase samples) or the computer search program³. Some results of the application of the JCPDS computer interpretation of typical environmental samples will be discussed.

EXPERIMENTAL

All x-ray fluorescence measurements were made using a Siemens SRS-1 wave length-dispersive spectrometer. In all cases, excitation was provided by a chromium target x-ray tube operated at 50 kV. In most cases, the sample was mixed 3:1 with a binder mix. Reduction of x-ray fluorescence data was effected by the XRF-11 fundamental parameters program (Criss Software) executed on a PDP-11 computer.

The powder diffraction patterns were obtained using a Siemens type F diffractometer with a copper x-ray tube operated at 35 kV. Samples were pulverized until able to pass a 400 mesh sieve. Samples were either backloaded onto a glass slide or applied to a glass slide as a slurry in amyl acetate. Interpretation and search of powder diffraction patterns was performed by the JCPDS search program, run on a UNIVAC 1100.

RESULTS AND DISCUSSION

For the evaluation of x-ray fluorescence data processed by the fundamental parameters (FP) program it was necessary to compare results with those for a sample which was rigorously characterized. The NBS 1633a fly ash satisfied this requirement. Only five single analyte standards and one double analyte standard were used and these differed in elemental composition from the unknowns by factors of two to seventy. The results for the fly ash analysis are shown in Table 1. The relative error ranged from 2% for calcium to 22% for sulfur.

Table 1. Elemental Composition in NBS SRM 1633a Fly Ash

Element	Accepted Comp. (%)	XRF-FP Comp. (%)	Standard Comp. (%)	Standard Phase	Error (%)
O	41.9	50.0			19
Al	14 ^a , 14.0 ³	12.1	52.9	Al ₂ O ₃	13
Si	22.8 ^b	26.0	46.8	SiO ₂	14
S	0.27 ^a	0.21	23.6	CaSO ₄	22
K	1.88 ^b	1.68	34.7	K ₂ CO ₃	10
Ca	1.11 ^b	1.08	29.4	CaSO ₄	2
Ti	0.80 ^a , 0.84 ³	0.83	60.0	TiO ₂	3
Fe	9.40 ^b	7.91	69.9	Fe ₂ O ₃	15

^aNBS information value.

^bNBS certified value.

The oxygen accepted value for the fly ash was calculated assuming all the major elements were present as oxides. The XRF-FP program generated the oxygen value by difference.

In the analysis of fuels by XRF, there is a complication in that the major elements carbon, hydrogen and nitrogen cannot be determined by XRF. Consequently, logical assumptions were sought which could simplify the determination yet produce reasonable values for those elements for which XRF data were available. For the determination of NBS 1635 coal, the standard was NBS 1632 coal. In the first set of analyses, hydrogen was set at 3 percent, nitrogen at 1 percent and the following carbon variations in SRM 1632 were specified: 0, 50, 64% (NBS accepted value), and 70%. Table 2 shows the results of this study. For comparison of the results, attention will be focused on phosphorus, whose behavior was quite typical. The NBS value for phosphorus was 0.012%. The calculated values for P were 0.013, 0.014, and 0.015% respectively for 50, 64 and 70% carbon - all slightly high but reasonable. However, if no carbon is assumed in the standard only 0.006% P was obtained. Another analysis was performed, specifying the correct carbon composition in the standard (64%) and the unknown (58.9%). The resulting calculation gave 0.027% P. This study concludes that it is necessary to make a rough assumption of carbon composition in the standard but that constraining the carbon composition in the unknown leads to significant errors in elemental composition.

In another study, results from XRF were compared with those from atomic absorption spectroscopy (AAS), differential pulse polar-

Table 2. Elemental Composition (%) in NBS SRM 1635 Coal Using SRM 1632 Coal as Standard

Element	Specified % C in SRM 1632				Specified Correct % C in 1632 and 1635	True 1635 Composition
	0%	50%	64%	70%		
C	90.5	92.4	92.3	92.4	58.9	58.9
Mg	0.041	0.106	0.110	0.108	0.119	0.098
Al	0.269	0.290	0.300	0.300	0.350	0.320
Si	3.370	0.619	0.420	0.652	1.03	0.900
P	0.006	0.013	0.014	0.015	0.027	0.012
S	0.416	0.394	0.421	0.431	0.838	0.330
Cl	0.025	0.008	0.009	0.009	0.021	0.010
K	0.117	0.014	0.015	0.016	0.039	0.009
Ca	0.128	0.487	0.531	0.549	1.49	0.560
Ti	0.103	0.017	0.019	0.019	0.069	0.020
Fe	0.970	0.132	0.146	0.152	0.625	0.239

ography (DPP), ion chromatography (IC), neutron activation analysis (NAA) and spark source mass spectrometry (SSMS) for a particulate sample from a copper smelter (Table 3). For this study, only one standard per element was used in the XRF analysis. If the true value for each element is taken as the mean of the values from all of the methods used for that element then the errors for the XRF analysis are 2, 4 and 5% respectively for cadmium, lead and antimony. The worst case was iron with an error of 55% average. For this set of elements the average error was 22%.

The JCPDS computer search program was used to identify phases containing the major elements in the sample. In all XRD analyses, elemental composition from XRF was specified to the search program. The program searches for line matches, then performs a sequential subtraction of each selected phase from the total unknown pattern. Phases that do not significantly alter the unknown pattern after this subtraction are "rejected." Other "accepted" phases are ranked by means of a "reliability factor". An "average" match has a reliability factor of 40-50, while a perfect fit would have a reliability factor of 100. Output for the copper smelter sample is shown in Table 4. The arsenic phase was identified as arsenic trioxide. Lead sulfate and cadmium sulfate were found, but later rejected by the multiple subtraction scheme. These and other rejections of likely phases could be due to a variety of factors, including pro-

Table 3. Elemental Composition (%) in Copper Smelter Electrostatic Precipitator Particulate Catch

Element	AAS	DPP	IC	NAA	SSMS	XRF	Standard Comp. (%)	Standard Phase
Al						11.03	52.9	Al ₂ O ₃
Si						1.15	46.8	SiO ₂
S						5.73	23.6	CaSO ₄
K					0.23	0.16	34.7	K ₂ CO ₃
Ca					0.16	0.09	29.4	CaSO ₄
Fe	2.19				3.12	4.31	69.9	Fe ₂ O ₃
Cu	5.88	6.23		2.90	7.92	2.25	59.3	Brass
Zn	2.19	1.85		2.90	2.40	2.01	35.7	Brass
As			31.2		13.10	41.00	75.7	As ₂ O ₃
Pb	5.25	5.71			18.20	10.22	86.6	PbO ₂
Sb				1.56	2.68	2.28	83.5	Sb ₂ O ₃
Cd	0.23				0.39	0.32	87.5	CdO

Table 4. Phases in Copper Smelter ESP Particulate from XRD

Phases Identified	Reliability of Accepted Phases	% Lines Matched Rejected Phases
As_2O_3	57	-
ZnSb_2SO_4	19	-
$\text{Sb}_2(\text{SO}_4)_3$	15	-
CuFeS_2	14	-
K_2O	10	-
PbSO_4	-	83
CdSO_4	-	71

gram parameter selection, preferred orientation of the sample, low concentration of rejected phase in unknown, and differences between the unknown phase and the JCPDS standard phase patterns. Tables 4, 5 and 6 also show the percentage of lines present for rejected but likely phases.

The XRF and XRD procedures were also applied to several other samples of environmental interest including a dual alkali scrubber sample. The only elements detected in scrubber solids by XRF were Na, S and Ca. The major by-product anticipated in the process is the hemihydrate of calcium sulfite. This species was readily identified by the JCPDS search. The other species shown in Table 5 are consistent with the chemistry of the scrubbing process.

Table 6 lists the results of XRF and XRD applied to an iron

Table 5. Phases and Elemental Composition of Dual Alkali Scrubber Solids

XRD Phases Identified	Reliability of Accepted Phases	% Lines Matched Rejected Phases	Element	XRF (%)
$\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$	60	-	Na	9.2
$\text{Na}_2\text{Mg}(\text{CO}_3)_2$	21	-	S	22.4
$\text{Ca}(\text{OH})_2$	20	-	Ca	24.1
$\text{CaCO}_3 \cdot \text{H}_2\text{O}$	10	-		
MgO	3	-		
Na_2SO_4	-	75		
NaHCO_3	-	67		

Table 6. Phases and Elemental Composition of Iron Smelter ESP Particulate

XRD Phases Identified	Reliability of Accepted Phases	% Lines Matched Rejected Phases	Element	XRF (%)
Fe_2O_3	63	-	O	34.1
K_2SO_4	39	-	Mg	1.29
$\text{Pb}_2(\text{SO}_4)_3$	24	-	Al	6.93
PbGa_2O_4	18	-	Si	2.81
$\text{Fe}_4(\text{As}_2\text{O}_{11})$	10	-	P	0.14
MgSiO_3	-	88	S	1.65
MgSO_4	-	80	K	0.58
CaAlSiO_6	-	75	Ca	7.95
			Ti	0.09
			Fe	44.4

smelter electrostatic precipitator (ESP) sample. The phase of the major element, iron, was identified as ferric oxide by the JCPDS search of the powder diffraction data. The combination of these techniques again yields results that are consistent with the known processes involved.

CONCLUSIONS

In general, the fundamental parameters program has proven to be quite capable of yielding meaningful results when applied to the analysis of environmental samples. Relative errors ranged from 2 to 20% for a variety of sample types. This accuracy was obtained using only one readily available pure compound (usually a simple inorganic oxide) as a standard per element determined. The advantage of this approach to a laboratory that receives a variety of "unique" samples is apparent. Additionally, the JCPDS computer search of powder diffraction data of environmental samples was shown to contribute to the speciation of the complex samples that are encountered in environmental assessments.

1. J. W. Criss, Fundamental Parameters Calculations on a Laboratory Microcomputer, Advances in X-ray Analysis, 23:93, Plenum Publishing Corp., 1980.
2. G. G. Johnson, Jr., "User Guide", Publ. by JCPDS, 1975.
3. E. S. Gladney, Analytica Chimica Acta, 118:385 (1980).

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